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Effects of alpha-zirconium phosphate on thermal degradation and flame retardancy of transparent intumescent fire protective coating

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ABSTRACT

Organophilic alpha-zirconium phosphate (OZrP) was used to improve the thermal and fire retardant behaviors of the phenyl di(acryloyloxyethyl)phosphate (PDHA)-triglycidyl isocyanurate acrylate (TGICA)-2-phenoxyethyl acrylate (PHEA) (PDHA-TGICA-PHEA) coating. The morphology of nanocomposite coating was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The effect of OZrP on the flame retardancy, thermal stability, fireproofing time and char formation of the coatings was investigated by microscale combustion calorimeter (MCC), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), laser Raman spectroscopy (LRS) and scanning electric microscope (SEM). The results showed that by adding OZrP, the peak heat release rate and total heat of combustion were significantly reduced. The highest improvement was achieved with 0.5 wt% OZrP. XPS analysis indicated that the performance of anti-oxidation of the coating was improved with the addition of OZrP, and SEM images showed that a good synergistic effect was obtained through a ceramic-like layer produced by OZrP covered on the surface of char.

1. Introduction

The protection of materials against fire has become an important issue in the construction industry. The use of flame retardant coating is one of the easiest, economical and the most efficient ways to protect materials against fire [1,2], and it is easily processed and could be used onto metals [3], polymers [4], textiles [5] or woods [6]. It presents two main advantages: it can prevent heat from penetrating and flames from spreading; moreover, it does not modify the intrinsic properties of the materials (e.g. the mechanical properties) [7,8].

In general, flame retardant coatings can be classified into two groups: non-intumescent coating and intumescent coating. Intumescent flame retardant coatings are made up of intumescent flame retardant (IFR) system, binder and fillers. The intumescent flame retardant system is usually composed of three active ingredients: an acid source (generally ammonium polyphosphate), a carbon source (such as pentaerythritol) and a blowing agent (most often melamine). Upon heating, the three active ingredients and the binder swell and form a thermal insulation multicultural layer. Intumescent flame retardant coatings attract more and more interests due to its excellent fireproof performance.

UV-curing, which effectively and instantaneously converts a usually liquid, low-viscosity resin into a polymerized and cross-linked solid polymer network, has become a well-accepted technology in polymer science [9,10]. Beneficial properties, such as rapid cured rate, reduced solvent emission, moderate curing condition, and the ability to coat heat-sensitive devices and circuits make photo-curable compositions attractive for many electronic applications [11,12]. Hence, a preferred and efficient method of intumescent flame retardant coating is its application of UV-cured technology. To improve the fire-resistant performance of the intumescent char of the flame retardant coatings, recently some synergistic agents such as nanoparticles [13–16] were used. In this study, we reported a layered phosphate, alpha-zirconium phosphate (α-Zr$(HPO_4)_2\cdot H_2O$, α-ZrP), which acted as a "solid acid" that could catalyze dehydrogenation of the polymers and enhance some performance of polymers, such as Liu et al. [17], Wang et al. [18] and Lu et al., [19]. The protons between layers of α-ZrP can exchange with many cations. α-ZrP was organically modified by an ammonium salt bearing long alkyl chains [hexadecyl trimethyl ammonium bromide (CTAB)] [20]. Organophilic α-ZrP (OZrP) could stabilize the carbon backbone of the PP and increase char residue through promoting an early cross-linking reaction of the PP carbon chain [21], which indicates that they might be used as modifiers to improve the thermal stability of the UV-flame retardant coating. However, according to our knowledge, up to now there is no research on this topic.

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In this paper, a synergistic agent, OZrP, was introduced into UV-curable systems. The FR consisted of phosphorus monomer (PDHA) and triglycidyl isocyanurate acrylate (TGICA). The main attention of this paper was focused on the synergistic effect in flame retardant coatings. The thermal properties and fire retardancy of nanocomposite coatings were evaluated with thermogravimetric analysis, thermogravimetric analysis/infrared spectrometry and microscale combustion calorimeter. The enhancement of thermal stability and the improvement of flame retardancy were observed. The charring structure was further characterized by scanning electron microscopy and laser raman spectroscopy.

2. Experimental

2.1. Materials

2-Phenoxyethyl acrylate (PHEA, as shown in Fig. 1) was supplied by Tianjin Tianjiao Company. OZrP powder was prepared by hydrothermal synthesis under the optimum condition according to our previous work [20]. PDHA was synthesized using phenyl dichlorophosphate (PDPC) and 2-hydroxyethyl acrylate (HEA) [22]. TGICA was synthesized using acrylic acid and triglycidyl isocyanurate [23]. The molecular formulas of PDHA and TGICA were shown in Fig. 1. Tetrahydrofuran (THF) was purchased from Shanghai Chemical Reagents Company in China. 2-Hydroxy-2-methyl-1-phenyl-1-propanone (Darocur1173), kindly supplied by Ciba Specialty Chemicals, was used as a photoinitiator.

2.2. Preparation of the samples

To prepare PDHA/TGICA/PHEA/OZrP nanocomposite, a certain amount of OZrP powder was dispersed in the solution containing PDHA, TGICA and PHEA (listed in Table 1) using ultrasonic treatment for 3 h, and then stirred for another 24 h at ambient temperature.

Table 1
Formulations of the flame retardant coatings.

Sample	Composition (phr)			OZrP (phr)
	PDHA	TGICA	PHEA	
OZrP0	35	35	30	0
OZrP1	35	35	30	0.5
OZrP2	35	35	30	1
OZrP3	35	35	30	3

2.3. UV irradiation process of PDHA/TGICA/PHEA/OZrP nanocomposite

The samples were UV cured with UV irradiation equipment (80 W/cm^2, made by Lantian Co.) in the presence of 4 wt% Darocur 1173. The UV irradiation was carried out in the air atmosphere.

2.4. Measurements

X-ray diffraction (XRD) analysis was carried out on sample at room temperature by a Japan Rigaku D/max-rA X diffraction meter (30 kV, 10 mA) with Cu ($\lambda = 1.54178$ Å) irradiation at the rate of 2°/min in the range of 1–10°.

Transmission electron microscopy (TEM) images were obtained on a Jeol JEM-100SX transmission electron microscope with an acceleration voltage of 100 kV. The TEM specimens were cut at room temperature using an ultramicrotome (Ultracut-1, UK) with a diamond knife from nanocomposite films. Thin specimens, 50–80 nm, were collected in a trough filled with water and placed on 200 mesh copper grids.

GOVMARK MCC-2 microscale combustion calorimeter (MCC) was used to investigate the combustion behavior of the UV-cured film. In this system, about 5 mg samples of UV-cured film

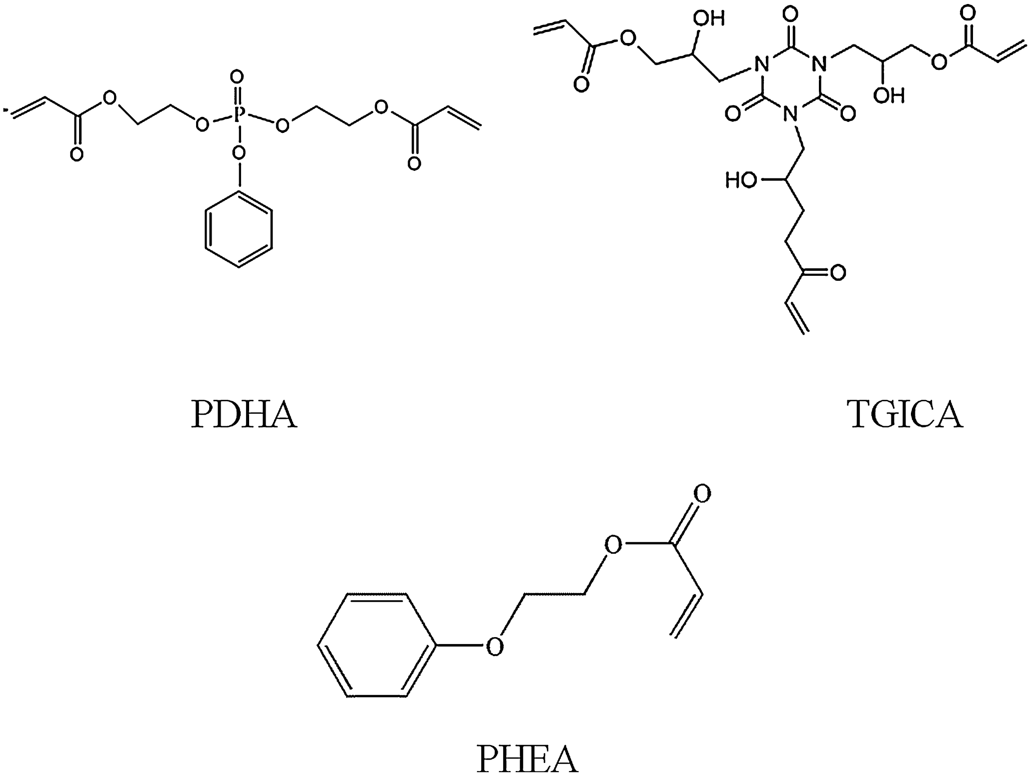

Fig. 1. The molecular structures of PDHA, TGICA and PHEA.